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Abstract: In the absence of a certified reference material, a robust microwave-assisted acid digestion procedure followed by inductively coupled plasma - mass spectrometry (ICP-MS) was developed to quantify rare earth elements (REEs) in fluidized-bed catalytic cracking (FCC) catalysts and atmospheric fine particulate matter (PM2.5). High temperature (200 °C), high pressure (200 psig), acid digestion (HNO<sub>3</sub>, HF, and H<sub>3</sub>BO<sub>3</sub>) with 20 minute dwell time effectively solubilized REEs from six fresh catalysts, a spent catalyst, and PM2.5. This method was also employed to measure 27 non-REEs including Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Mo, Cd, Cs, Ba, Pb, and U. Complete extraction of several REEs (Y, La, Ce, Pr, Nd, Tb, Dy, and Er) required HF indicating that they were closely associated with the aluminosilicate structure of the zeolite FCC catalysts. Internal standardization using <sup>115</sup>In quantitatively corrected non-spectral interferences in the catalyst digestate matrix. Inter-laboratory comparison using ICP-optical emission spectroscopy (ICP-OES) and instrumental neutron activation

analysis (INAA) demonstrated the applicability of the newly developed analytical method for accurate analysis of REEs in FCC catalysts. The method developed for FCC catalysts was also successfully implemented to measure trace to ultra-trace concentrations of La, Ce, Pr, Nd, Sm, Gd, Eu, and Dy in ambient PM<sub>2.5</sub> in an industrial area of Houston, TX.

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May 24, 2006

Professor P.K. Dasgupta,  
Editor, *Analytica Chimica Acta*  
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Dear Prof. Dasgupta,

Enclosed please find a manuscript titled “Microwave-assisted extraction of rare earth elements from petroleum refining catalysts and ambient fine aerosols prior to inductively coupled plasma – mass spectrometry” for peer-review prior to possible publication in *Analytica Chimica Acta*. I have co-authored this manuscript with Mr. Pranav Kulkarni, my doctoral student and Dr. David Mittlefehldt, Space Scientist at the NASA Johnson Space Center in Houston. Dr. Mittlefehldt manages NASA’s instrumental neutron activation analysis (INAA) laboratory and performed the INAA measurements reported in this manuscript. I will serve as the corresponding author.

***Analytical novelty of the research.*** We have developed and quantitatively verified microwave digestion and inductively coupled plasma – mass spectrometry techniques to accurately and precisely measure all naturally occurring rare earth elements in the aluminosilicate matrices of fluidized-bed catalytic cracking catalysts and atmospheric fine particles. One important basis of our research is that to date, no certified reference material is available for these zeolite-based catalysts. Additionally, existing reference materials for atmospheric particles such as SRM 1648 from the National institute of Standards and technology only include four rare earths (La, Ce, Sm, and Eu) and that too only as uncertified elements. We have quantitatively validated ICP-MS results with independent analyses using ICP-OES and INAA. The digestion and analysis method developed herein successfully captured 3 orders of magnitude variation in REEs (e.g. Dy in  $\text{pg/m}^3$  and La in  $\text{ng/m}^3$ ) demonstrating its suitability to analyze trace to ultra-trace REEs levels in atmospheric  $\text{PM}_{2.5}$ .

***Key findings and significance to real sample matrices.*** Note that all matrices (fresh catalysts, spent catalyst, atmospheric particulate matter, etc.) considered in this manuscript pertain directly to real-world samples. Importantly, we have included a sample of spent catalyst obtained from Shell Oil Company because during usage catalysts get poisoned and deposited with coke. Complete extraction of several REEs (Y, La, Ce, Pr, Nd, Tb, Dy, and Er) required HF indicating that they were closely associated with the aluminosilicate

structure of the zeolite FCC catalysts. Internal standardization using  $^{115}\text{In}$  quantitatively corrected non-spectral interferences in the catalyst digestate matrix. The method developed for FCC catalysts was also successfully implemented to measure trace to ultra-trace concentrations of La, Ce, Pr, Nd, Sm, Gd, Eu, and Dy in ambient  $\text{PM}_{2.5}$  in an industrial area of Houston, TX. 8 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy) were detected in  $\text{PM}_{2.5}$  samples from Houston's Ship Channel area. We demonstrate that the loss of FCC catalyst from the refinery was the primary source of REEs in ambient atmospheric fine particles and that increase in  $\text{PM}_{2.5}$  mass was predominantly caused by the loss of FCC catalyst during the "upset" event.

I appreciate the opportunity to publish in *Analytica Chimica Acta*. As the corresponding author, please contact me at [chellam@uh.edu](mailto:chellam@uh.edu) if I can provide additional information.

Sincerely,

Shankar Chellam  
Associate Professor  
Department of Civil and Environmental Engineering  
Department of Chemical Engineering

# Microwave-assisted extraction of rare earth elements from petroleum refining catalysts and ambient fine aerosols prior to inductively coupled plasma – mass spectrometry

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## Abstract

In the absence of a certified reference material, a robust microwave-assisted acid digestion procedure followed by inductively coupled plasma – mass spectrometry (ICP-MS) was developed to quantify rare earth elements (REEs) in fluidized-bed catalytic cracking (FCC) catalysts and atmospheric fine particulate matter (PM<sub>2.5</sub>). High temperature (200 °C), high pressure (200 psig), acid digestion (HNO<sub>3</sub>, HF, and H<sub>3</sub>BO<sub>3</sub>) with 20 minute dwell time effectively solubilized REEs from six fresh catalysts, a spent catalyst, and PM<sub>2.5</sub>. This method was also employed to measure 27 non-REEs including Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Mo, Cd, Cs, Ba, Pb, and U. Complete extraction of several REEs (Y, La, Ce, Pr, Nd, Tb, Dy, and Er) required HF indicating that they were closely associated with the aluminosilicate structure of the zeolite FCC catalysts. Internal standardization using <sup>115</sup>In quantitatively corrected non-spectral interferences in the catalyst digestate matrix. Inter-laboratory comparison using ICP–optical emission spectroscopy (ICP-OES) and instrumental neutron activation analysis (INAA) demonstrated the applicability of the newly developed analytical method for accurate analysis of REEs in FCC catalysts. The method developed for FCC catalysts was also successfully implemented to measure trace to ultra-trace concentrations of La, Ce, Pr, Nd, Sm, Gd, Eu, and Dy in ambient PM<sub>2.5</sub> in an industrial area of Houston, TX.

**Keywords:** Microwave digestion, FCC catalysts, ICP-MS, INAA, petroleum refining, rare earth elements, lanthanides, PM<sub>2.5</sub>

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## 1. INTRODUCTION

Trace metals in atmospheric fine particles ( $PM_{2.5}$ ) have been proposed as a dose metric to better explain adverse health outcomes arising upon exposure to  $PM_{2.5}$  compared with total mass [1]. Trace elements in  $PM_{2.5}$  can serve as the basis of receptor-oriented modeling [2, 3] and also provide important information for epidemiological studies. To date, the vast majority of studies on trace elements in ambient aerosols have only focused on the main groups and main transition series (*d*-block) elements e.g. [4-9]. Only a very select number of studies have focused on rare earth elements (REEs) e.g. [10, 11], which comprise the elements Y, La, and the lanthanides (Ce – Lu) [12].

It is crucial to monitor REEs in  $PM_{2.5}$ , especially in industrial environments, because they are the sole tracers to track fluidized-bed catalytic cracking (FCC) emissions from petroleum refining operations [10, 11, 13]. Even though La and Ce have been reported for vehicle  $PM_{2.5}$  emissions [14, 15] and occasionally in ambient PM [4, 9], analyzing other lanthanides is essential to identify loss of FCC catalysts from petroleum refineries and their contributions to ambient  $PM_{2.5}$ .

A major challenge in quantifying REEs emissions from refineries is the lack of a certified reference material for FCC catalysts [16]. Additionally, because REEs are present only in trace to ultra-trace levels in ambient  $PM_{2.5}$  they are difficult to measure accurately and precisely, necessitating either high temperature – high pressure microwave assisted acid ( $HNO_3+HF+H_3BO_3$ ) digestion followed by inductively coupled plasma - mass spectrometry (ICP-MS) [5, 9] or instrumental neutron activation analysis (INAA) [13]. Even though INAA is a non-destructive technique that can accurately quantify selected REEs, (1) it cannot quantify all REEs, (2) has a long time-lag between start of the experiment and final data compilation, (3) requires a high level of infrastructure, (e.g. irradiation facility), and (4) produces low-level nuclear waste that remains radioactive for decades. In contrast, accurate and precise trace-level analysis of several elements including REEs at high throughput, relatively low cost, and creating less waste disposal issues can be achieved using microwave digestion followed by ICP-MS. One advantage of INAA is that minimal sample preparation is required – grinding, homogenizing and splitting – and this makes the technique ideal for validation of methods that require more elaborate sample processing such as ICP-MS.

To date, REEs have been quantified in natural biological, industrial, and geological samples such as peat, plant, soil, sediment, tissue, meteorites, ores, etc. [17-24]. In contrast, FCC catalysts are anthropogenic, which are manufactured by incorporating REE cations in a zeolite support, and contain higher levels of siliceous matter. Therefore, previously developed methods cannot be directly applied to them because of matrix-induced complications and difficulties in solubilizing the aluminosilicate backbone of zeolites.

The principal objective of this research is to develop a robust method for accurate and precise quantitation of all naturally occurring REEs (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) present in FCC catalysts and ambient PM<sub>2.5</sub>. Twenty seven other elements (Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Mo, Cd, Cs, Ba, Pb, and U) were also measured. A combination of HNO<sub>3</sub>, HF, and H<sub>3</sub>BO<sub>3</sub> was employed to digest several representative catalysts (six fresh and one spent) and PM<sub>2.5</sub> in a microwave oven followed by ICP-MS. The newly developed method was validated by independent analysis using inductively coupled plasma – optical emission spectrometry (ICP-OES) and INAA.

## **2. EXPERIMENTAL WORK**

**2.1. Catalysts.** Samples of six different FCC zeolites (SMR1-SMR6) used in a wide range of petroleum refining operations were obtained from the world's leading catalyst manufacturer (Grace Davison Inc., Columbia, MD). All fresh catalysts were odorless and white to brown in color, in the form of a fine powder with bulk densities ranging between  $\sim 0.45 - 1.00 \text{ g/cm}^3$ . Scanning electron micrographs of two representative fresh catalysts are given in Figure 1a and 1b. Similar to other fresh catalysts, SMR1-SMR6 were spherical having smooth surfaces [25]. A sample of spent zeolite catalyst was also employed, because during operation, high temperature fractionation and coke deposition changes catalyst composition and morphology. This sample was obtained from the Shell Deer Park Refining Company's Catalytic Cracking Unit in June 2003 and was collected after cyclone separators have removed it from the generator. The spent catalyst was also an odorless fine powder but was dark gray in color. Figure 1c shows that in contrast to the fresh catalysts, its surface was nodular and rough, caused by chemical contamination and abrasion. Substantial differences in the morphology between the fresh and spent catalysts demonstrate the need to

include both types for development of a robust analytical method that will be applicable to all FCC zeolite catalysts. All samples were dried at 80 °C for 4 h in a clean oven and stored in a desiccator before use.

**2.2. Ambient fine particles.** PM<sub>2.5</sub> samples were collected between May 25, 2001 and September 4, 2001 from a monitoring station (HRM3) located in an industrial park surrounded by numerous petroleum refineries in the Houston Ship Channel area. Twenty five samples were collected on Teflon membrane filters using a multi-channel fine-particle sampler fitted with an AIHL cyclone and in-line filter holders. The volumetric airflow rate was set to 0.6 m<sup>3</sup>/hr using orifice plates to fractionate PM<sub>2.5</sub>. After a 24 h collection period, filters were sealed inside sampling petri dishes and frozen in the laboratory until further analysis. Additional information on the geographic location of HRM3, sampling methods, and equipment have been reported by us recently [11, 26].

One additional ambient PM<sub>2.5</sub> sample was also collected during an “increased air emissions event” or “industrial upset” from monitoring site “C15/A115” in the Houston Ship Channel area on September 3, 2005. Figure 2 depicts hourly PM<sub>2.5</sub> concentrations at this site during and just before the upset event. As seen, the air quality exceeded the Federal limit (National Ambient Air Quality Standard) during the upset and was categorized as ‘unhealthy’ by the Texas Commission on Environmental Quality (TCEQ). Based on the information given by the TCEQ, the upset was caused by a malfunctioning wet gas compressor in a local oil refinery, releasing an estimated 92 kg PM<sub>2.5</sub>, 412 kg CO, 382 kg NO<sub>x</sub>, 1340 kg SO<sub>2</sub>, and 1535 kg volatile organic compounds into the atmosphere.

**2.3. Reagents and Standards.** 65% HNO<sub>3</sub> and 99.99% H<sub>3</sub>BO<sub>3</sub> (Suprapurgrade, EM Science, Gibbstown, NJ), 48% HF (PPB/Teflon grade, Fluka, Milwaukee, WI) were employed for sample digestions. REE preconcentrations prior to ICP-OES analyses (see §2.8) were performed using *n*-heptane, (AR grade, Fluka, Milwaukee, WI), *n*-octanol (99+% HPLC grade Fluka, Milwaukee, WI), diester mix of 65% bis(2-ethylhexyl) hydrogen phosphate and 35% 2-ethylhexyl dihydrogen phosphate (Tokyo Kasei Co. Ltd., Portland, OR).

Ultra-high purity water from a commercial system (Max159 Modulab, U.S. Filter Corporation, Lowell, MA) was used for all solution preparations and dilutions. Multi-element ICP-MS and ICP-OES



calibration solutions were prepared using 1 mg/L working standard solutions obtained by mixing 10 mg/L single element standards (High Purity Standards, Charleston, SC). The composition of the background solution used for reagent blanks, internal standards, and calibration was kept identical to the final digestate (see §2.4) in order to avoid errors related to matrix inconsistencies. Two working standards were prepared, one containing 15 REEs (Pm cannot be analyzed because it has no naturally occurring stable isotope [12]) and another containing the 27 non-REEs. To correct for instrumental drift and plasma fluctuations, all solutions were spiked with an internal standard (5 µg/L  $^{115}\text{In}$ ) prior to ICP-MS and ICP-OES analysis. Storage of standards and reagents and labware cleaning procedures has been described elsewhere by us [5].

**2.4. Closed vessel acid digestion.** Samples were digested in a programmable 1200 W microwave (MARS 5, CEM Corp., Matthews, NC) using 100 mL Teflon-lined vessels rated at 210 °C and 350 psig (HP-500 Plus, CEM Corp., Matthews, NC). Pressure and temperature profiles in the vessels were digitally acquired at a frequency of 1/3 Hz during the heating and cooling cycles on an external computer to better evaluate the effects of experimental variables on sample digestion.

The effect of HF volume on digestion was evaluated for all the catalysts using a fixed volume (5 mL) of  $\text{HNO}_3$ . 50 mg of each catalyst were aliquoted into six separate Teflon vessels and varying the volume of HF in each vessel (0.00, 0.05, 0.10, 0.30, 0.50, or 1.00 mL). The vessels were capped, placed in the microwave system, and digested using a two-stage procedure. In the first stage, the temperature was ramped to 200 °C with the application of 600 W power followed by a dwell time of 20 min. Only for the case of 0.3 mL HF, lower temperature settings of 150 °C and 175 °C were also evaluated. The vessels were allowed to cool for 60-90 minutes, and then vented and opened.

In the second stage, any remaining HF was masked and fluoride precipitates were re-dissolved by adding stoichiometric excess of  $\text{H}_3\text{BO}_3$  (5% m/v solution corresponding to eight times the HF volume) because several elements including REEs and few alkaline earth elements form insoluble fluoride precipitates leading to insufficient recovery. (Not incorporating  $\text{H}_3\text{BO}_3$  after using HF may result in REE concentrations below ICP-MS method detection limits, e.g. [9].) The vessels were recapped and heated again to set points of 200 °C, 200 psig, with 20 min dwell time. After cooling, a 4.29 mL aliquot of the

digestate was diluted with ultrapure water to a final volume of 100 mL, in order to obtain a 2% HNO<sub>3</sub> concentration. Catalyst digestates were further diluted 1, 10, 100, or 1000 fold as necessary to measure all elements within the ICP-MS and ICP-OES dynamic range.

Ambient PM<sub>2.5</sub> filters were also digested using the same two-stage technique determined to be optimal for FCC catalysts (200 °C, 200 psig, and 20 min dwell time). Acid volumes were proportionately reduced for these measurements since total PM<sub>2.5</sub> mass on each of the filters was only in the range of 0.2-0.5 mg. Additional discussion of acid volumes used to digest ambient PM<sub>2.5</sub> is given in §3.5. H<sub>2</sub>O<sub>2</sub> addition [5, 6, 8] was not necessary because a clear solution was obtained with HNO<sub>3</sub>, HF, and H<sub>3</sub>BO<sub>3</sub> alone.

**2.5. ICP-MS.** The ICP-MS (Elan 6000, Perkin-Elmer, Norwalk, CT) was tuned using a solution of 10 µg/L of Ba, Cd, Ce, Cu, Ge, Mg, Pb, Rh, Sc, Tb, and Tl in 2% HNO<sub>3</sub> to verify mass resolution. This was followed by X-Y adjustment, argon gas flow and lens optimization, and an instrument performance check. Nebulizer and auxiliary gas flows were separately adjusted along with the torch position to minimize Ce and Ba oxide formation rates and maximize <sup>103</sup>Rh count rates. The mass spectrometer was calibrated separately using two external standards solutions, one consisting of 15 REEs and the other having 27 non-REEs. The final digestate after appropriate dilution and the internal standard solution (5 µg/L <sup>115</sup>In) were mixed prior nebulization. The instrument was calibrated separately for REEs and non-REEs, which were then analyzed in two different runs. Platinum cones were cleaned periodically in a 2% HNO<sub>3</sub> solution by ultrasonication for 2 min at room temperature. Instrumental operating parameters are summarized in Table 1.

**2.6. ICP-OES.** An ICP-OES (4300 DV Perkin Elmer instruments, Shelton, CT) housed in another laboratory located at Rice University, Houston, TX was used to compare ICP-MS results obtained for each catalyst sample. The same blanks, multi-element external standards, and internal standard solutions used for ICP-MS were also used with the ICP-OES. Operating conditions and spectral lines used for REE analysis are also listed in Table 1. Operating parameters especially, nebulizer gas flow and the ICP generator power were all optimized to minimize spectral overlaps of the blank corrected emission intensities for all 42 elements monitored herein.

**2.7. INAA.** Instrumental neutron activation analysis was performed in the Gamma-ray Spectroscopy Laboratory (GSL) of NASA/Johnson Space Center, Houston, TX. Because FCC catalysts contained  $10^3$ - $10^6$  times the light REE concentrations compared with the meteorite, lunar, and planetary samples normally analyzed in the GSL; they represented a serious potential contamination hazard for the laboratory and posed a significant analytical challenge. Hence, routine analysis procedures were modified to reduce neutron self-shielding (some REEs can have very high neutron capture cross sections) and mitigate the potential for laboratory contamination.

Plastic vials containing ~2 g of each catalyst sample were shipped to GSL/NASA from which duplicate or triplicate splits, each ~20 mg were analyzed. The samples were weighed into 0.3 mL polyethylene vials and heat sealed. One sample of NIST 1633a coal fly ash was used as the primary standard for all elements except Na, for which International Working Group AN-G anorthosite was used as the standard.

Catalyst samples, standards, and controls (see §2.9) were irradiated for 2 hours at a thermal neutron flux of  $6.6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  at Texas A&M University Nuclear Science Center, College Station, TX. For the first three count sets, samples and reference materials were counted in the GSL on two ~15% efficiency intrinsic Ge detectors. Later counting was done using two ~50% efficiency intrinsic Ge detectors in the low-level counting room. A series of four counts 2-3, 3-7, 16-21, and 36-47 days after irradiation were performed to acquire data on nuclides with differing half-lives listed in Table 2. Net peak areas were calculated from the raw spectral data using an updated version of the TEABAGS program [27]. Interference corrections, concentrations of elements, and initial data evaluation were carried out using additional in-house programs. Following automatic data reduction, the data were manually investigated and necessary background corrections and additional interference corrections were employed.

**2.8. REE preconcentration.** Tb, Ho, Tm, and Lu concentrations in final digestates were increased above ICP-OES detection limits by first extracting them in 20 mL of a diester mix of 65% bis(2-ethylhexyl) hydrogen phosphate and 35% 2-ethylhexyl dihydrogen phosphate in *n*-heptane (P0261, Tokyo Kasei Co. Ltd.) [28, 29]. REEs were back-extracted from the organic phase to the aqueous phase by adding 10 mL of

octanol and 5 mL HCl. Traces of octanol were removed by washing the aqueous phase three times with 5 mL of *n*-heptane. The acid solution containing REEs was then evaporated to near dryness on a hot plate at 40 °C. Finally, the sample residues were dissolved in 4 – 10 mL of 2% HNO<sub>3</sub> prior to ICP-OES resulting in 10 – 25 fold enrichment for Tb, Ho, Tm, and Lu.

**2.9. Quality assurance.** In the absence of a certified FCC catalyst reference material, several quality control and quality assurance measures were employed to stringently evaluate the newly developed analytical methods. First, a known concentration of each REE was spiked in aluminosilicate zeolite powder (ICN19390280, Fisher Scientific, Houston, TX) as well as each of the seven FCC catalysts and aged for 90 days. These spiked samples were digested using the optimal procedure and analyzed by ICP-MS to obtain REEs recoveries. Secondly, another catalyst type, SRM 2556 (recycled pellet automobile catalyst, NIST, Gaithersburg, MD) with specified amounts of La and Ce was also used to ensure the validity of our ICP-MS methods. Thirdly, we compared REE concentrations obtained from ICP-MS with ICP-OES and INAA.

For INAA, splits of ~50 mg each of three certified reference materials (NIST 1633a coal fly ash, US Geological Survey BHVO-1 Hawaiian basalt, and International Working Group AN-G anorthosite), were used as controls.

Additionally, each digested PM<sub>2.5</sub> sample was analyzed in triplicate by ICP-MS along with a fourth replicate, to which known amounts of REEs were added to monitor matrix spike recoveries. Finally, to better capture variability in petroleum refining operations (catalyst type, size, and quantity for various end products) and meteorology, PM<sub>2.5</sub> samples were not collected on consecutive days but spaced over a 100-day period.

### **3. RESULTS AND DISCUSSION**

**3.1. Experimental reproducibility.** Digestions and ICP-MS measurements were repeated on different dates during the course of our work using the newly developed optimal analytical method (see §3.5) for each of the catalysts. In all cases, no statistically significant differences ( $p = 0.05$ ) in REE concentrations was observed. Hence, each catalyst sample was homogenous and individual samples could be used separately for method development. Additionally, the coefficient of variation was always < 10 % demonstrating excellent precision

in our measurements. These results demonstrate that all our digestion and ICP-MS experimental protocols were consistent and highly reproducible allowing a quantitative comparison of results generated over the entire duration of this study.

For INAA, elemental concentrations in the controls and reference materials were predominantly within  $1\sigma$  of the recommended values. Figure 3 compares the INAA results on different splits of individual catalyst samples. For the 6 REEs shown, determinations on replicate splits also agreed well statistically; of the 54 ratios shown, 50 (93%) were within the  $2\sigma$  (95%) limit indicating that the analyzed splits of each sample were representative and INAA provided reproducible measurements.

**3.2. Temperature and pressure during microwave digestion.** Microwave set points of 150 °C and 175 °C resulted in a black residue, demonstrating incomplete sample dissolution. Because a clear solution was obtained for 200 °C it was always selected as the set-point for future digestions.

Because temperature has a greater influence on solid sample dissolution than pressure [30], care was taken to ensure that it always remained the controlling parameter during microwave operation. Temperature and pressure profiles in the Teflon vessels for the optimal method are depicted in Figure 4. As observed, the set-point of 200 °C was achieved with  $\sim 140$  psig and 145 psig in the first and second stages respectively. Higher pressures during the second stage were caused by increased liquid volume due to  $\text{H}_3\text{BO}_3$  addition.

Figure 4c depicts the maximum pressure attained in the second stage with varying acid volumes for SMR1. Because first stage pressures remained  $\sim 140$  psig even when different HF volumes were employed, it is not shown herein. The pressure in the extraction vessels can be seen to increase with digestate volume resulting from larger HF and  $\text{H}_3\text{BO}_3$  additions, but never reached the 200 psig set-point. Hence, temperature controlled all the digestions resulting in reproducible and precise extractions. Similar results were obtained for all other catalysts and  $\text{PM}_{2.5}$  where set point of 200 °C always yielded a colorless solution, indicating complete dissolution of the solid samples.

**3.3. Mass spectral interferences and isotope selection.** Potential interferences from polyatomic ions, isobaric overlaps, and relative abundances were all considered before selecting the most appropriate REE isotope for ICP-MS analysis. Depending on the plasma operating conditions, REEs can form oxides ( $\text{MO}^+$ )

and hydroxides ( $\text{MOH}^+$ ), which along with barium oxides can potentially cause severe spectral interferences [31]. Hence, nebulizer gas flow and RF power were carefully optimized by trial and error during instrument tuning to maximize the signal intensity (measured as  $^{103}\text{Rh}$  counts) and minimize the oxide formation rates (measured as  $\text{CeO/Ce}$  counts), which was also frequently checked during analysis. Table 3 summarizes the REE isotopes chosen in this study for ICP-MS analysis along with their possible major interferences.

Even with the optimized instrumental conditions (Table 1), and maintaining  $\text{MO}^+/\text{M}^+ < 5\%$  and  $\text{MOH}^+/\text{M}^+ < 1.5\%$ , Nd and Gd, which were present in high levels in FCC catalysts induced mass spectral overlaps (Table 3) resulting in significant systematic errors (15-45%) for Tb, Yb, and Lu, which were present in much lower concentrations. Therefore, matrix-induced polyatomic interferences for the monitored REE isotopes were corrected by obtaining oxide and hydroxide counts for single element solutions of Te, Ba, Ce, Nd, Gd, Sm, Pr, Eu, and Tb prepared in the reagent blank solution. These elements were selected because they constitute the major REE interferences. Their concentrations were kept in the same range as that expected in catalyst samples. Intensities (I) for Nd, Sm, Eu, Gd, Tb, Er, Yb, and Lu were mathematically corrected by applying correction equations, e.g.

$$\left( I_{^{153}\text{Eu}}^{\text{corrected}} \right)_{\text{sample}} = \left( I_{^{153}\text{Eu}}^{\text{measured}} \right)_{\text{sample}} - \left( I_{^{137}\text{Ba}}^{\text{measured}} \right)_{\text{sample}} \left( \frac{I_{^{137}\text{Ba}^{16}\text{O}}^{\text{measured}}}{I_{^{137}\text{Ba}}^{\text{measured}}} \right)_{\text{single element solution}} .$$

**3.4. Non-spectral interferences and internal standard selection.** Non-spectral ICP-MS interferences for REEs arising from biological and environmental samples have been previously corrected using  $^{102}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{115}\text{In}$ , and  $^{185}\text{Re}$  as internal standards [17, 18, 24]. However, FCC zeolite catalysts are predominantly composed of aluminosilicates (see §3.5) and the complete composition of their digestate matrix has not yet been established. Therefore, we evaluated several potential internal standards to accurately measure REEs.

0.0, 0.5, 1.0, 1.5, and 2.0 %  $\text{HNO}_3$  solutions each having 0.08 % HF and 0.06 %  $\text{H}_3\text{BO}_3$  (identical to the reagent blank) were spiked with all REEs in the similar concentration range as anticipated in the final catalyst digestate. Changes in REEs signal intensities in these solutions with varying  $\text{HNO}_3$  concentrations were monitored along with each potential internal standard counts. Typical results obtained are depicted in Figure 5 for one light ( $^{139}\text{La}$ ) and one heavy ( $^{175}\text{Lu}$ ) REE along with each of the four internal standards after

normalizing intensities by that of the aqueous solution (0% HNO<sub>3</sub>). Increasing HNO<sub>3</sub> concentrations suppressed signal intensities presumably due to salt deposition and viscosity-induced changes in aerosolization efficiency in the nebulizer even though concentrations of REEs and internal standards were maintained constant. REE signal intensities were reduced by 25–35% in the final digestate (2% HNO<sub>3</sub>) as compared to the aqueous solution. Additionally, similar suppression trends can be seen in Figure 5 for <sup>103</sup>Rh, <sup>115</sup>In, and REEs suggesting that either would be appropriate for internal standardization. In contrast, <sup>102</sup>Ru and <sup>185</sup>Re exhibited a different trend compared with REEs demonstrating that they would not be effective internal standards for the FCC catalyst matrix. Hence, even though both <sup>103</sup>Rh and <sup>115</sup>In could be used, <sup>115</sup>In was chosen as the internal standard for REE quantitation in the catalyst digestate matrix using ICP-MS because its first ionization energy (558 kJ/mol) is within the range of all REEs (523–623 kJ/mol). Note that Rh has higher first ionization energy (720 kJ/mol).

**3.5. Effect of HF amount.** 0 mL, 0.05 mL, 0.1 mL, 0.3 mL, 0.5 mL, or 1.0 mL of HF was added to the first stage of microwave digestion to assess REE dissolution/extraction from FCC catalysts. Results from SMR1 and the spent catalyst are shown in Table 4. Method detection limits were also determined using the technique described in [32] and expressed in µg/Kg of FCC catalyst. As observed, lighter REE (Y, La, Ce, Pr, and Nd) concentrations increased most noticeably whereas Sm, Tb, Dy, Er, and Yb increased moderately as HF volume increased from 0 mL to 0.05 mL to 0.1 mL to 0.3 mL. However, HF volumes > 0.3 mL did not enhance dissolution of these REEs. In contrast, HF addition did not impact Eu, Gd, Ho, Tm, and Lu concentrations. Similar results were obtained for other catalysts SMR2 – SMR6.

These results demonstrate the need to employ HF to completely extract REEs from the aluminosilicate matrix of FCC catalysts. The acid mixture containing 5 mL HNO<sub>3</sub>, 0.3 mL HF, and 2.4 mL H<sub>3</sub>BO<sub>3</sub> (method 4 in Table 4) necessitated a dilution factor of 3588 (mL/g sample) to achieve 2% HNO<sub>3</sub> in the final digestate prior to ICP analysis. Excessive HF did not enhance REE extraction but the concomitant H<sub>3</sub>BO<sub>3</sub> addition increased total dissolved solids content deteriorating ICP-MS sensitivity. Hence, method 4 was chosen as the optimal digestion method, and employed in all future digestions. Moreover, quantitative recoveries of the two REEs (La 98±3 % and Ce 98±2 %) from a closely related catalyst (SRM 2556) lends

further validity to using method 4 to extract REEs from FCC catalysts.

Chondrite normalized [33] REE concentrations in catalysts revealed several anomalies indicating substantial anthropogenic contributions (see Figure 6). Ce and Eu anomalies have been previously reported in natural geological samples owing to their different oxidation states and redox geochemistry [34]. However, anomalies for Gd, Er, and Yb in Figure 6 demonstrates alterations in natural REE abundances in FCC catalysis probably arising during the stripping of REE cations in the zeolite matrix [35]. Similar trends in CI normalized REE concentrations were obtained for ambient  $PM_{2.5}$ . Unusual positive anomalies distinguish the matrix of FCC catalysts and ambient atmospheric fine particles from samples such as peat, plant, soil, sediment, tissue, etc. that preserve natural REE abundances necessitating a different dissolution/ICP-MS method for anthropogenic samples.

Table 5 compares concentrations of non-REEs in 6 fresh catalysts and the spent catalyst obtained using the newly developed method. As expected from the aluminosilicate backbone of zeolitic catalysts employed in this study, Al and Si were most dominant together accounting for 36 – 54% of the mass. K, Na, and Ti were also present in very high levels collectively constituting 1.4 – 3.4% of the measured mass. Concentrations of Ni, V, Co, Cu, and Mo were substantially increased ( $\sim 2 - 50$  fold) in the spent catalyst compared with fresh catalysts demonstrating poisoning. Chemical contamination by these metals beyond the range of fresh catalysts coupled with morphological changes (Figure 1) not only reduces catalytic activity during refining but validates our choice of including a spent catalyst for method development research reported herein.

**3.6. Predigestion matrix spike recoveries.** Table 6 shows REE spike recoveries from all seven FCC catalysts and the zeolite powder along with the amount of spike added to each sample. Excellent recoveries with  $< 15\%$  error confirm the applicability of digestion method 4 to extract REEs from the solid catalyst samples.

**3.7. Comparison of ICP-MS and ICP-OES.** All FCC catalyst samples were digested using the optimal method and also analyzed by ICP-OES. Typical results obtained are depicted in Figure 7 in the form of a bivariate scatter plot. Excellent agreement between ICP-MS and ICP-OES measurements of REEs can be



observed in two fresh catalysts (SMR1 and SMR2) and the spent catalyst. Similar results were obtained for SMR3 – SMR6. Paired t-tests and regression analysis revealed no statistical differences between the two methods at 95% confidence for all catalyst samples. Hence, REE analyses of the digestate using ICP-MS were accurate and precise. Note that using ICP-OES only allows the verification of our ICP-MS results. Because ICP-OES and ICP-MS were performed on the same sample digestate, this comparison does not validate the digestion methodology.

**3.8. Comparison of ICP-MS and INAA.** Using the INAA represents a more stringent validation of the newly developed method because it does not require sample digestion. To evaluate both sample digestion and ICP-MS analysis of the newly developed method (method 4 in Table 4), direct REE measurements from solid samples were performed using INAA. 12 elements including 8 REEs (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) and 4 non-REEs (Na, Fe, Co, and Ba) were quantified by INAA.

Table 7 summarizes quantitative deviation between ICP-MS and INAA in all catalysts in terms of relative percent deviation (RPD) [36, 37] calculated as

$$RPD (\%) = \frac{|X_{ICP-MS} - X_{INAA}|}{\frac{1}{2}(X_{ICP-MS} + X_{INAA})} \times 100$$

where X is the element chosen for comparison. As depicted in Table 7, good agreement was observed for most of the elements (<20% RPD) in all catalysts. Similar to previous reports of REE analyses from peat, plant, rock, and rice, higher RPDs (>20%) were observed for Tb, Yb, and Lu [17, 38]. Hence, care should be taken prior to report these three REEs from several matrices. Further, as observed from Figure 8, ICP-MS and INAA agreed very closely (except for La in spent catalyst). Results summarized in Figure 8 and Table 7 demonstrates that INAA results agreed well with ICP-MS measurements for most REEs and substantiate the newly developed method.

**3.9. Analysis of ambient fine particulate matter.** The optimal digestion technique (method 4 in Table 4) was also used to extract REEs from atmospheric PM<sub>2.5</sub> samples prior to ICP-MS analysis. HF and H<sub>3</sub>BO<sub>3</sub> volumes were reduced proportionately to digest the lower PM mass collected on each filter (0.2-0.5 mg) compared to the 50 mg FCC catalyst mass employed for method development (see §3.5). A minimum 3 mL

HNO<sub>3</sub> was necessary to monitor temperature profiles within the digestion vessels employed (HP500 plus) and to prevent potential localized overheating of the liners.

Using this procedure, 8 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy) were detected in PM<sub>2.5</sub> samples from Houston's Ship Channel area, which are depicted in Figure 9 in the form of a time series. Matrix spike recoveries of each of these elements were in the range 84 – 108% indicating accurate analysis. Enrichment of these REEs in PM<sub>2.5</sub> has already been quantitatively traced back to catalyst emissions from petroleum refining operations [11, 13]. Further, Figure 9 depicts that La, Ce, Pr, Nd, Sm, Gd, and Dy profiles were in phase, following each other very closely, and even peaking on the same days (June 3 and August 14). Statistically significant and positive correlations ( $p=0.01$ ) were also observed between each of these REEs signifying a common emission source (FCC catalysts). In contrast, because Eu concentrations in FCC catalysts and local soil were in the same range [11], its profile was not in phase with other REEs as it was emitted by at least these two sources. Further, as seen in Figure 9, the digestion and analysis method developed herein successfully captured 3 orders of magnitude variation in REEs (e.g. Dy in pg/m<sup>3</sup> and La in ng/m<sup>3</sup>) demonstrating its suitability to analyze trace to ultra-trace REEs levels in PM<sub>2.5</sub>.

**3.10. REEs as markers of FCC catalysts emissions.** Figure 10 compares REE concentrations measured during the “increased air emissions event” on 09/03/2005 and the spent catalyst. Strong positive correlations were observed for light REEs, viz. La, Ce, Nd, Pr, Gd, Sm, Eu in Figure 10a ( $R^2=0.99$ ) and for heavy REEs, viz. Tb, Dy, Ho, Er, Tm, Yb, and Lu in Figure 10b ( $R^2=0.89$ ). Additionally, the REE abundance sequence in the spent catalyst and the ambient PM<sub>2.5</sub> sample were similar (La>Ce>Nd>Pr>Gd>Sm>Dy>Eu~Er~Yb~Lu~Tb~Ho). These two observations suggest that the loss of FCC catalyst from the refinery was the primary source of REEs in ambient atmospheric fine particles.

Next, enrichment factors were calculated using Nd as the reference because it was present in very high levels in the spent catalyst compared to the local soil [11]:

$$\text{Enrichment factor (X)} = \frac{[X]_{\text{PM}_{2.5}} / [\text{Nd}]_{\text{PM}_{2.5}}}{[X]_{\text{spent catalyst}} / [\text{Nd}]_{\text{spent catalyst}}}$$

Enrichment factors for Y, La, Ce, Pr, Sm, Gd, Dy, Tb, Er, and Yb were all close to unity indicating that the

refining malfunction contributed FCC catalyst particles to the local atmosphere. Finally, the ratio of La and Ce, which were the two dominant REEs in the spent catalyst and ambient PM<sub>2.5</sub> during the emission event were very similar (11.2 and 13.0 respectively) lending further evidence that the increase in PM<sub>2.5</sub> mass was predominantly caused by the loss of FCC catalyst during the “upset” event in the refinery.

#### 4. CONCLUSIONS

Closed vessel microwave acid digestion with set points at 200 °C, 200 psig, and 20 min dwell time using 5 mL HNO<sub>3</sub> (65%), 0.3 mL HF (48%) and 2.4 mL H<sub>3</sub>BO<sub>3</sub> (5% m/v) quantitatively extracted 15 REEs and 27 other elements from 50 mg of FCC catalysts. The same digestion method with reduced acid volumes (3 mL HNO<sub>3</sub>, 3 µL HF, and 24 µL H<sub>3</sub>BO<sub>3</sub>) could also identify 8 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy) in ambient atmospheric fine particles. Results reported herein are valuable to on-going efforts at the National Institute of Standards and Technology to develop a FCC catalyst standard reference material [16]. Additionally, analyzing REEs would enhance air quality monitoring studies by providing clues to the origin of ambient aerosols in daily ambient PM<sub>2.5</sub> samples [11] as well as increased PM<sub>2.5</sub> concentrations following “upsets”. Hence, REEs analysis is recommended for quantitative apportionment of petroleum refining operations to PM<sub>2.5</sub> mass in industrialized environments.

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**Table 1.** Operating conditions and instrumental setup for ICP-MS and ICP-OES

	ICP-MS	ICP-OES
Instrument	Elan 6000 (Perkin Elmer, Norwalk, CT, USA), Gem-Tip crossflow nebulizer, Rytan spray chamber, four-channel peristaltic pump (Gibson, Model Minipuls III)	Perkin Elmer 4300 DV, SCD detector, Cyclonic spray chamber, Gem-Tip cross flow nebulizer
RF power	1300 W	1150 W
Nebulizer gas flow	0.85-1.00 L/min. optimized for each analysis to maximize the counts and minimize the oxide formation	0.85 L/min.
Auxiliary gas flow	0.8 L/min	0.8 L/min
Lens voltage	6.5 V	Not applicable
Cones	Pt sampler (1.1 mm orifice id) Pt skimmer (0.8 mm orifice id)	Not applicable
Sampling parameters	AS-90, Perkin-Elmer autosampler, sample uptake rate 1 ml/ min, rinsing time 60 s (2% HNO <sub>3</sub> ), signal read delay time 35 s	AS-93 plus, Perkin-Elmer autosampler, sample uptake rate 1.5 ml/ min, rinsing time 60 s (2% HNO <sub>3</sub> )
Data acquisition	Peak hopping mode, 50 sweeps per reading, 3 readings per replicate, 3 replicates, dwell time 100 ms	3 reading per replicate, 3 replicates, wavelengths: La (398.852 nm), Ce (413.764 nm), Pr (390.844 nm), Dy (353.170 nm), Er (337.271 nm), Eu (381.967 nm), Gd (342.247 nm), Ho (345.600 nm), Nd (406.109 nm), Sm(359.260 nm), Tb (350.917 nm), Yb (328.937 nm), Tm (313.126 nm), Lu (261.542 nm), Y (371.029 nm)
Time	3-4 min/sample	2-3 min/sample

**Table 2.** Nuclides for REEs utilized in INAA along with their half-lives and the specific photopeak energies used in the assay

Nuclide	<sup>140</sup> La	<sup>141</sup> Ce	<sup>147</sup> Nd	<sup>153</sup> Sm	<sup>152</sup> Eu	<sup>160</sup> Tb	<sup>169</sup> Yb	<sup>175</sup> Yb	<sup>177</sup> Lu
Half-life (days)	1.68	32.6	11	1.95	4821	72.1	32	4.19	6.71
Gamma-ray energy (keV)	328.8, 487, 815.9, 1596.5	145.4	531	103.2	778.9, 1408.1	298.6	177.2	282.5, 396.3	208.3

**Table 3.** Isotopes selected for ICP-MS analysis along with their major potential spectral interferences in HNO<sub>3</sub>-HF-H<sub>3</sub>BO<sub>3</sub> matrix (adapted from [18]).

Isotope	Abundance (%)	Main Interferences
<sup>89</sup> Y	100	<sup>178</sup> Hf <sup>++</sup>
<sup>139</sup> La	99.91	<sup>123</sup> Sb <sup>16</sup> O
<sup>140</sup> Ce	88.48	-
<sup>141</sup> Pr	100	-
<sup>146</sup> Nd	17.19	<sup>130</sup> Te <sup>16</sup> O
<sup>147</sup> Sm	15	<sup>130</sup> Ba <sup>16</sup> O <sup>1</sup> H
<sup>153</sup> Eu	52.2	<sup>137</sup> Ba <sup>16</sup> O, <sup>136</sup> Ba <sup>16</sup> O <sup>1</sup> H
<sup>158</sup> Gd	24.84	<sup>142</sup> Nd <sup>16</sup> O
<sup>159</sup> Tb	100	<sup>143</sup> Nd <sup>16</sup> O, <sup>142</sup> Nd <sup>16</sup> O <sup>1</sup> H
<sup>163</sup> Dy	24.9	<sup>147</sup> Sm <sup>16</sup> O
<sup>165</sup> Ho	100	<sup>149</sup> Sm <sup>16</sup> O, <sup>148</sup> Nd <sup>16</sup> O <sup>1</sup> H
<sup>166</sup> Er	33.60	<sup>150</sup> Nd <sup>16</sup> O, <sup>150</sup> Sm <sup>16</sup> O
<sup>169</sup> Tm	100	<sup>153</sup> Eu <sup>16</sup> O
<sup>172</sup> Yb	21.9	<sup>156</sup> Gd <sup>16</sup> O
<sup>175</sup> Lu	97.41	<sup>159</sup> Tb <sup>16</sup> O, <sup>158</sup> Gd <sup>16</sup> O <sup>1</sup> H

**Table 4.** Influence of HF volume in the digestion mixture on REE concentrations analyzed by ICP-MS. Results for one fresh FCC catalyst (SMR1) and one spent catalyst are shown. All concentrations (average  $\pm$  standard deviation) are in mg/Kg except method detection limits (MDLs), which are in  $\mu\text{g/Kg}$ .

		Method 1		Method 2		Method 3		Method 4		Method 5		Method 6	
		5 ml HNO <sub>3</sub>		5 ml HNO <sub>3</sub> + 0.05 ml HF + 0.4 ml H <sub>3</sub> BO <sub>3</sub>		5 ml HNO <sub>3</sub> + 0.1 ml HF + 0.8 ml H <sub>3</sub> BO <sub>3</sub>		5 ml HNO <sub>3</sub> + 0.3 ml HF + 2.4 ml H <sub>3</sub> BO <sub>3</sub>		5 ml HNO <sub>3</sub> + 0.5 ml HF + 4.0 ml H <sub>3</sub> BO <sub>3</sub>		5 ml HNO <sub>3</sub> + 1.0 ml HF + 8.0 ml H <sub>3</sub> BO <sub>3</sub>	
REE	MDL $\mu\text{g/Kg}$	SMR1	Spent catalyst	SMR1	Spent catalyst	SMR1	Spent catalyst	SMR1	Spent catalyst	SMR1	Spent catalyst	SMR1	Spent catalyst
<sup>89</sup> Y	2.982	16 $\pm$ 0.7	17.1 $\pm$ 1.1	33.7 $\pm$ 1.2	16.4 $\pm$ 1.3	20.5 $\pm$ 0.9	16.6 $\pm$ 0.6	22.0 $\pm$ 0.7	16.3 $\pm$ 0.8	22.3 $\pm$ 0.9	16.6 $\pm$ 0.8	22.1 $\pm$ 0.3	16.5 $\pm$ 0.6
<sup>139</sup> La	5.471	3022 $\pm$ 34	4378 $\pm$ 88	3415 $\pm$ 41	5180 $\pm$ 58	4384 $\pm$ 53	8647 $\pm$ 111	4596 $\pm$ 40	10017 $\pm$ 77	4597 $\pm$ 49	9970 $\pm$ 81	4591 $\pm$ 56	9987 $\pm$ 73
<sup>140</sup> Ce	3.524	1816 $\pm$ 24	714 $\pm$ 64	2778 $\pm$ 20	720 $\pm$ 62	2964 $\pm$ 34	737 $\pm$ 80	3122 $\pm$ 29	770 $\pm$ 66	3130 $\pm$ 26	787 $\pm$ 63	3128 $\pm$ 19	770 $\pm$ 79
<sup>141</sup> Pr	4.792	467 $\pm$ 8	474 $\pm$ 25	545 $\pm$ 11	480 $\pm$ 18	541 $\pm$ 11	499 $\pm$ 22	568 $\pm$ 6	502 $\pm$ 27	566 $\pm$ 5	503 $\pm$ 13	567 $\pm$ 9	502 $\pm$ 11
<sup>146</sup> Nd	6.082	647 $\pm$ 12	515 $\pm$ 20	888 $\pm$ 17	658 $\pm$ 12	926 $\pm$ 14	691 $\pm$ 21	943 $\pm$ 8	699 $\pm$ 26	945 $\pm$ 7	699 $\pm$ 15	969 $\pm$ 12	698 $\pm$ 16
<sup>147</sup> Sm	3.169	117 $\pm$ 3	138 $\pm$ 7	121 $\pm$ 4	146 $\pm$ 4	116 $\pm$ 3	150 $\pm$ 6	114 $\pm$ 4	151 $\pm$ 6	122 $\pm$ 3	152 $\pm$ 8	123 $\pm$ 4	151 $\pm$ 4
<sup>153</sup> Eu	2.310	4.4 $\pm$ 0.2	5.1 $\pm$ 0.3	4.5 $\pm$ 0.3	5.1 $\pm$ 0.2	4.4 $\pm$ 0.2	5.2 $\pm$ 0.2	4.1 $\pm$ 0.1	5.3 $\pm$ 0.2	4.6 $\pm$ 0.3	5.4 $\pm$ 0.2	4.5 $\pm$ 0.4	5.4 $\pm$ 0.2
<sup>157</sup> Gd	4.175	105 $\pm$ 6	475 $\pm$ 6	102 $\pm$ 9	475 $\pm$ 4	100 $\pm$ 4	490 $\pm$ 8	106 $\pm$ 4	488 $\pm$ 11	108 $\pm$ 3	489 $\pm$ 9	106 $\pm$ 5	489 $\pm$ 5
<sup>159</sup> Tb	1.318	2.2 $\pm$ 0.1	2.9 $\pm$ 0.1	3.0 $\pm$ 0.0	3.9 $\pm$ 0.1	3.2 $\pm$ 0.1	3.9 $\pm$ 0.1	3.6 $\pm$ 0.6	4.0 $\pm$ 0.2	4.0 $\pm$ 0.4	4.3 $\pm$ 0.1	3.9 $\pm$ 0.2	4.1 $\pm$ 0.2
<sup>163</sup> Dy	2.993	8.8 $\pm$ 0.3	11 $\pm$ 0.6	8.8 $\pm$ 0.2	19.1 $\pm$ 1.1	11.4 $\pm$ 0.7	19.4 $\pm$ 0.9	12.3 $\pm$ 0.1	21.1 $\pm$ 1.6	12 $\pm$ 0.2	22.5 $\pm$ 1.4	12.6 $\pm$ 0.5	22.3 $\pm$ 1.0
<sup>165</sup> Ho	0.273	1.0 $\pm$ 0.0	1.0 $\pm$ 0.1	0.8 $\pm$ 0.1	1.0 $\pm$ 0.0	1.0 $\pm$ 0.0	1.0 $\pm$ 0.0	1.1 $\pm$ 0.1	1.3 $\pm$ 0.0	1.2 $\pm$ 0.1	1.4 $\pm$ 0.1	1.1 $\pm$ 0.1	1.4 $\pm$ 0.0
<sup>166</sup> Er	1.732	3.8 $\pm$ 0.2	4.2 $\pm$ 0.5	3.7 $\pm$ 0.2	4.0 $\pm$ 0.3	4.7 $\pm$ 0.3	4.2 $\pm$ 0.3	5.3 $\pm$ 0.5	6.2 $\pm$ 0.4	5.7 $\pm$ 0.4	6.4 $\pm$ 0.1	5.5 $\pm$ 0.4	6.3 $\pm$ 0.6
<sup>169</sup> Tm	0.647	0.2 $\pm$ 0	0.2 $\pm$ 0	0.2 $\pm$ 0	0.4 $\pm$ 0	0.2 $\pm$ 0.0	0.3 $\pm$ 0	0.3 $\pm$ 0.0	0.4 $\pm$ 0.0	0.3 $\pm$ 0.0	0.4 $\pm$ 0.0	0.3 $\pm$ 0.0	0.4 $\pm$ 0.0
<sup>172</sup> Yb	1.397	1.2 $\pm$ 0.1	1.9 $\pm$ 0.1	1.8 $\pm$ 0.1	2.6 $\pm$ 0.09	1.8 $\pm$ 0.1	2.4 $\pm$ 0.1	1.3 $\pm$ 0.2	7.1 $\pm$ 0.2	1.4 $\pm$ 0.1	8.2 $\pm$ 0.7	1.4 $\pm$ 0.2	6.6 $\pm$ 0.5
<sup>175</sup> Lu	0.812	0.1 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.0

In all cases a two stage digestion was performed with set points of 200 °C and 200 psig with 20 min. dwell time using 65% HNO<sub>3</sub>, 48% HF, and 5% H<sub>3</sub>BO<sub>3</sub>.

Method detection limits were calculated as three times the standard deviation of seven analyses of a digested reagent blank solution employed as in method 4 spiked with REEs of interest each at half the lowest concentration used to calibrate the ICP-MS instrument as suggested in [32].

**Table 5.** Non-REE elemental composition of FCC catalysts. All concentrations are in mg/Kg.

Isotope	Fresh catalyst concentration range (mg/Kg)	Spent catalyst (mg/Kg)
<sup>23</sup> Na	1,208 – 4,935	4,240 ± 278
<sup>24</sup> Mg	164 – 278	509 ± 5
<sup>27</sup> Al	114,000 – 289,000	245,000 ± 8180
<sup>28</sup> Si	221,000 – 268,000	200,000 ± 302,00
<sup>39</sup> K	6,336 – 23,287	20,600 ± 2,100
<sup>45</sup> Sc	19 – 28	37 ± 2
<sup>47</sup> Ti	3,819 – 9,019	9,109 ± 674
<sup>51</sup> V	35 – 72	445 ± 5
<sup>52</sup> Cr	52 – 124	133 ± 23
<sup>55</sup> Mn	9.1 – 22.1	27.0 ± 0.4
<sup>57</sup> Fe	2,737 – 4,838	5,984 ± 63
<sup>59</sup> Co	2.9 – 5.9	117 ± 2
<sup>60</sup> Ni	12 – 24	1,094 ± 12
<sup>63</sup> Cu	7 – 23	46.5 ± 0.2
<sup>68</sup> Zn	59 – 123	153 ± 2
<sup>69</sup> Ga	35 – 71	63 ± 1
<sup>75</sup> As	6.2 – 15.9	6.3 ± 0.0
<sup>77</sup> Se	14.9 – 56.3	28.6 ± 0.1
<sup>85</sup> Rb	2 – 4	2.5 ± 0.0
<sup>88</sup> Sr	35 – 105	53.0 ± 1.1
<sup>90</sup> Zr	47 – 78	66.3 ± 0.4
<sup>95</sup> Mo	1.1 – 2.2	12.2 ± 0.1
<sup>111</sup> Cd	< MDL (=0.5)	< MDL (=0.5)
<sup>133</sup> Cs	0.24 – 0.27	0.22 ± 0.06
<sup>137</sup> Ba	85 – 255	134.1 ± 2.1
<sup>208</sup> Pb	22 – 45	48 ± 1
<sup>238</sup> U	1.6 – 3.9	2.8 ± 0.1



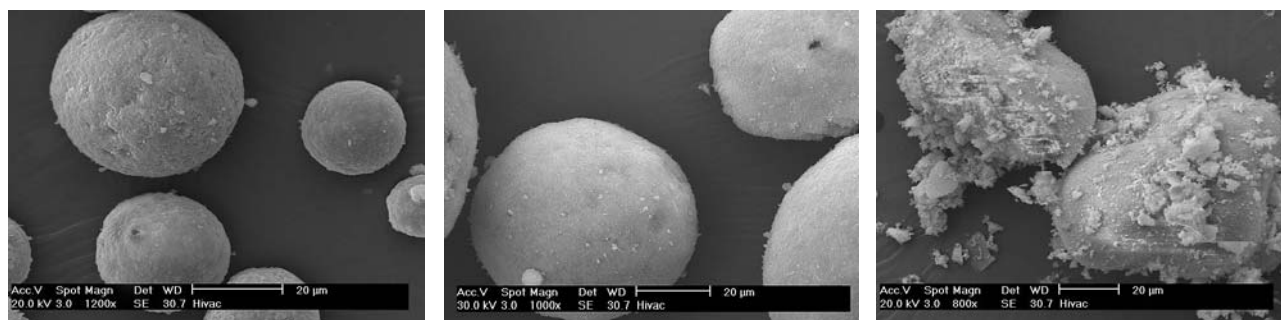
**Table 6.** REE spike recoveries (%) from aged FCC catalysts and zeolite.

Analyte	Concentration range in all 7 FCC catalysts (mg/kg)	Spike added (ng)	SMR1 (%)	SMR2 (%)	SMR3 (%)	SMR4 (%)	SMR5 (%)	SMR6 (%)	Spent catalyst (%)	Zeolite (%)
<sup>89</sup> Y	10.6 – 43.1	100	109±5	113±4.7	102±4	112±4	98±5	89±6	109±6	98±3
<sup>139</sup> La	4,597 – 10,452	40,000	96±6	108±4.7	112±3	113±4	109±4	110±5	112±3	102±4
<sup>140</sup> Ce	770 – 12378	40,000	88±8	101±4.8	103±5	94±3	96±4	95±6	92±7	98±6
<sup>141</sup> Pr	499 – 1696	5,000	93±4	95±4.6	92±6	93±9	90±10	90±4	95±4	95±3
<sup>144</sup> Nd	716 – 3,054	10,000	108±4	100±9.2	105±7	107±7	112±3	111±5	92±2	95±1
<sup>152</sup> Sm	26 – 271	700	99±1	101±8.0	102±11	103±3	100±4	105±4	104±9	104±3
<sup>153</sup> Eu	0.9 – 21.1	40	97±2	100±5.2	103±6	104±2	103±5	98±8	106±3	102±6
<sup>157</sup> Gd	65 – 1228	2,000	110±5	101±4.4	98±4	108±5	111±4	112±4	117±1	98±4
<sup>159</sup> Tb	3.2 – 13.7	40	106±5	86±0.9	104±2	89±2	88±1	85±4	107±2	103±2
<sup>162</sup> Dy	8.2 – 30.0	100	102±7	111±5.3	114±10	97±10	107±1	93±6	94±1	103±4
<sup>165</sup> Ho	0.7 – 2.3	5	105±3	106±8.4	112±13	109±27	108±9	107±3	107±8	98±1
<sup>166</sup> Er	4.3 – 13.7	50	105±4	99±8.1	90±10	93±11	109±4	106±5	87±4	102±1
<sup>169</sup> Tm	0.1 – 0.4	5	110±5	93±5.6	89±6	90±5	103±12	108±5	89±6	100±2
<sup>172</sup> Yb	0.8 – 14.9	25	92±3	90±4.6	112±4	106±5	108±5	109±5	105±3	102±1
<sup>175</sup> Lu	0.2 – 0.6	5	92±3	85±6.0	94±3	97±4	94±10	113±6	91±4	95±3

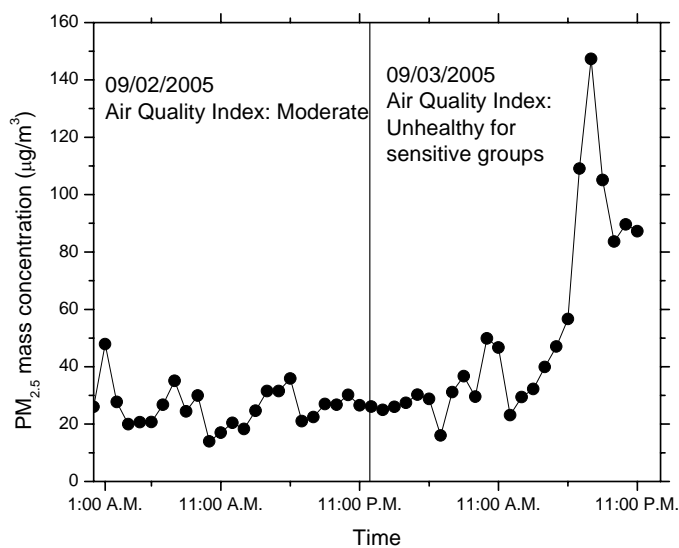
Spikes were added 90 days before microwave digestion with HNO<sub>3</sub> + HF + H<sub>3</sub>BO<sub>3</sub>. For each REE, average spike recovery and standard deviation of 3 – 6 measurements are reported.

**Table 7.** Inter-comparison of ICP-MS and INAA measurements in terms of relative percentage deviation.

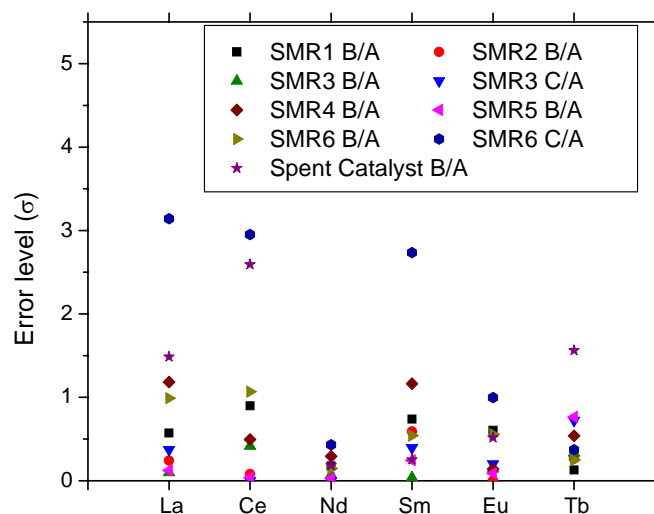
FCC catalysts	Relative Percentage Deviation, RPD (%)		
	<20%	20% - 40%	>40%
SMR1	La, Ce, Nd, Sm, Eu, Yb, Lu, Na, Co, Ba	Tb	
SMR2	La, Ce, Nd, Sm, Yb, Lu, Co, Ba	Tb, Lu, Na	
SMR3	La, Ce, Nd, Sm, Eu, Yb, Lu, Na, Co, Ba	Tb	
SMR4	La, Ce, Nd, Sm, Eu, Co, Ba	Tb, Lu, Na	Yb
SMR5	La, Ce, Nd, Sm, Eu, Lu	Yb	Tb
SMR6	La, Ce, Nd, Sm, Eu, Lu	Tb, Yb	Na
Spent	Nd, Sm, Eu, Lu, Na, Co	Tb	La, Ce, Yb



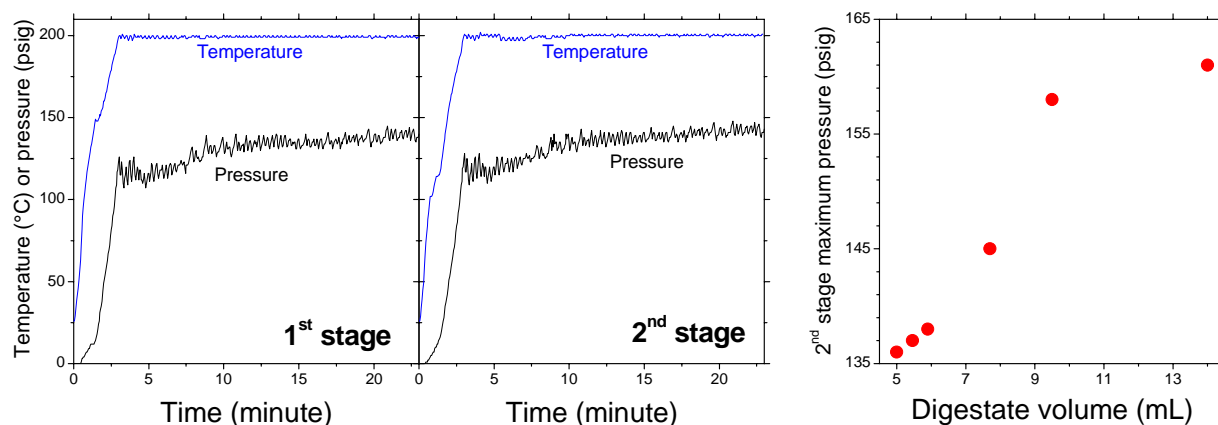
**Figure 1.** SEM images of typical fresh catalysts SMR1 and SMR2 (a and b respectively) and spent catalyst (c).



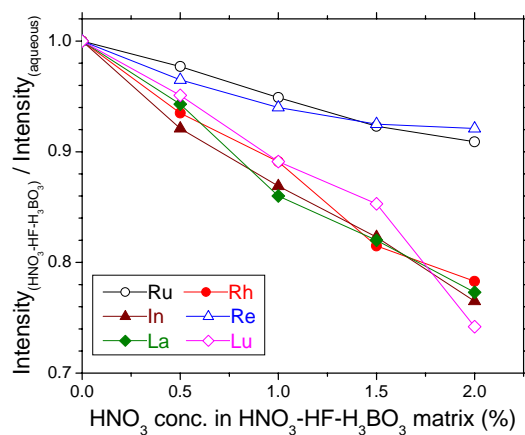
**Figure 2.** Hourly PM<sub>2.5</sub> concentrations during an “upset” at site “C15/A115” in the Houston Ship Channel area on September 2 and 3, 2005 provided by the Texas Commission on Environmental Quality.



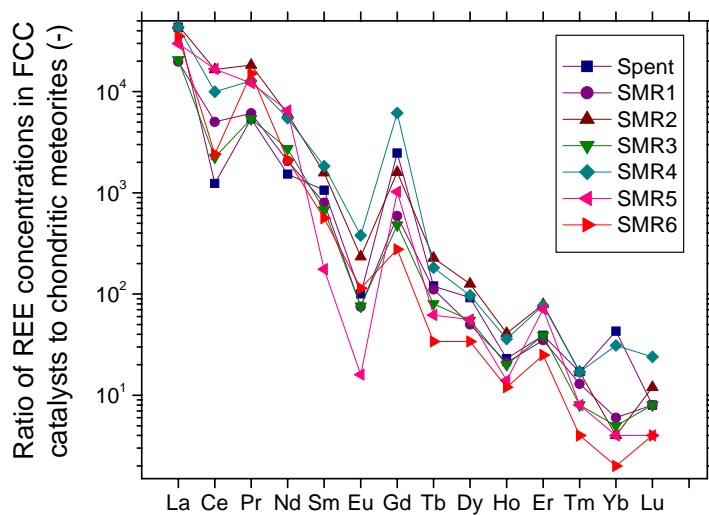
**Figure 3.** Error in INAA analysis REE measurements within duplicate or triplicate (A, B, and C) splits of individual zeolite catalysts. The errors are calculated using [39].



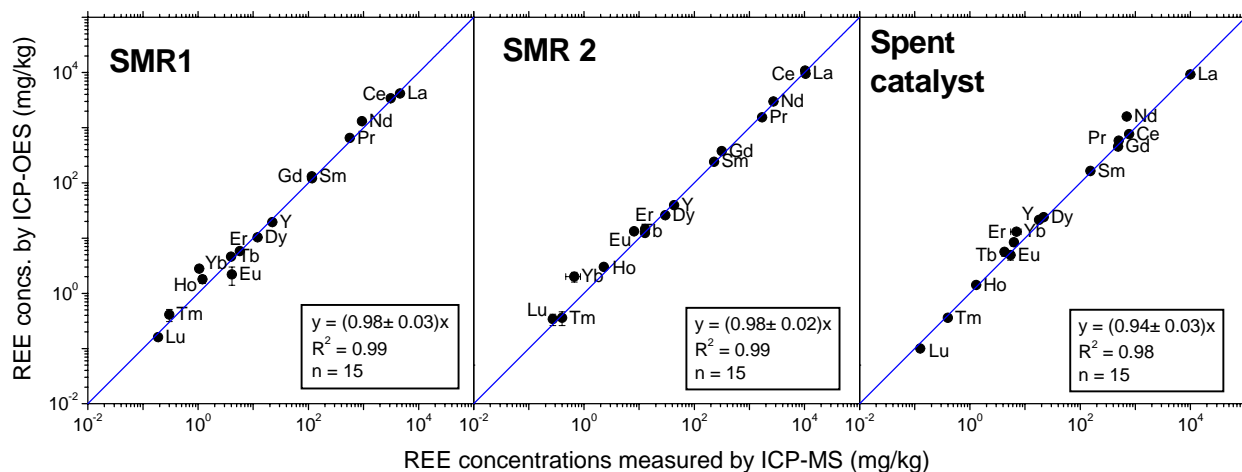
**Figure 4.** Temperature and pressure profiles during two-stage digestion of 50 mg SMR1 with 5 mL  $\text{HNO}_3$ , 0.3 mL HF, and 2.4 mL  $\text{H}_3\text{BO}_3$  with set points were 200 °C and 200 psig and dwell time of 20 minutes. The maximum pressure reached in the second digestion stage as a function of total acid volume is also shown.



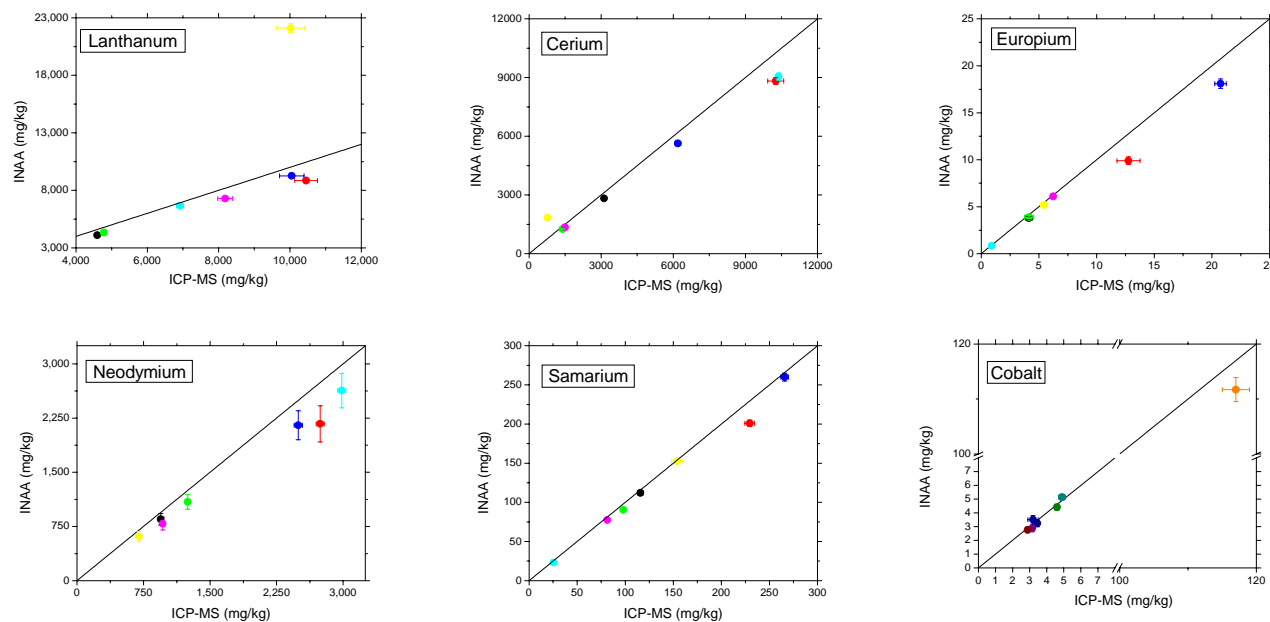
**Figure 5.** Effect of  $\text{HNO}_3\text{-HF-H}_3\text{BO}_3$  matrix on potential internal standards ( $^{102}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{115}\text{In}$ , and  $^{185}\text{Re}$ ) along with a representative light REE ( $^{139}\text{La}$ ) and a heavy REE ( $^{175}\text{Lu}$ ). All intensities have been normalized by that corresponding to ultrapure water.



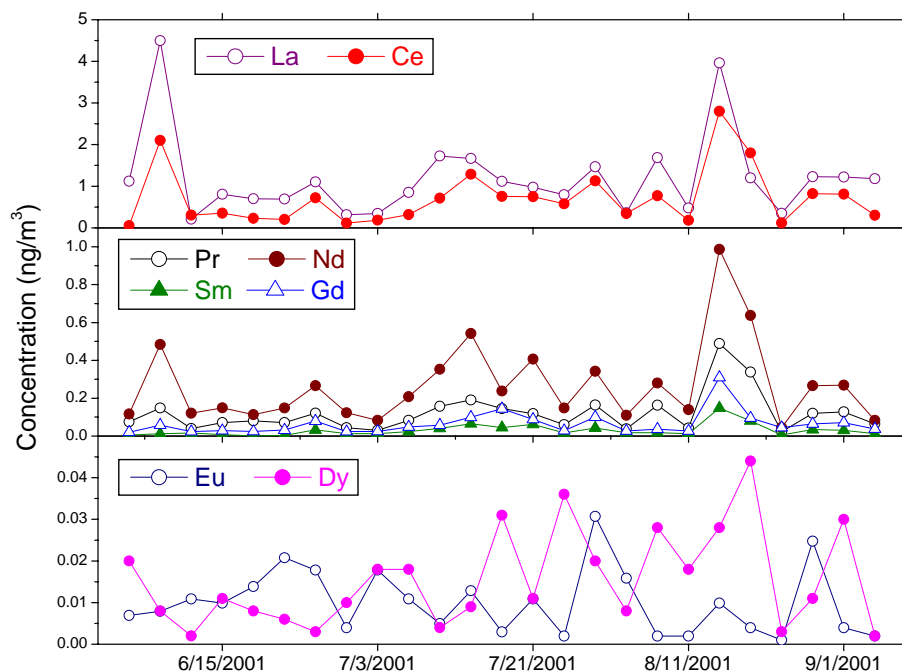
**Figure 6.** Chondritic normalized plot suggesting alteration in REE composition in FCC catalysts compared to natural abundances. Chondritic meteorites concentrations obtained from [33].



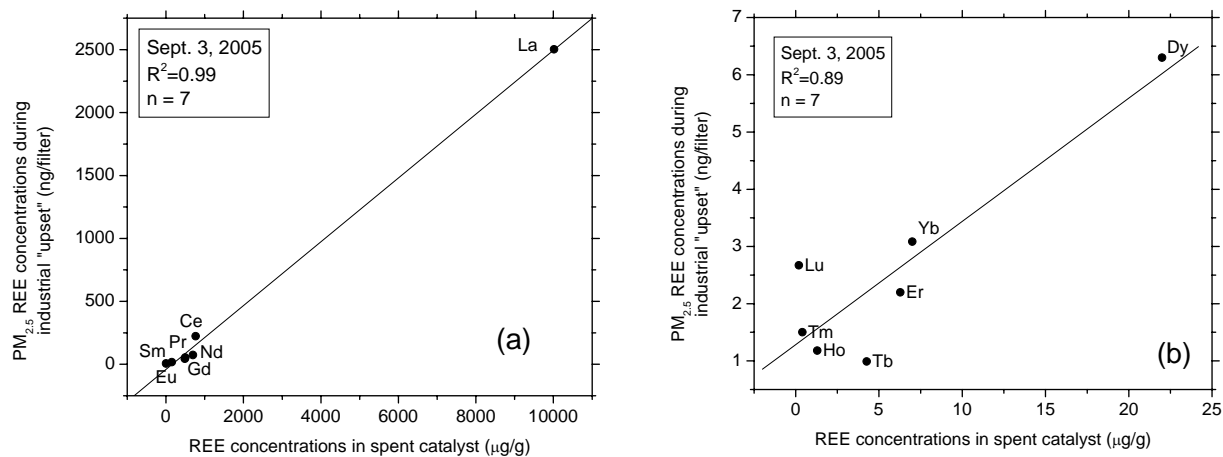
**Figure 7.** Scatter plots of REE concentrations in FCC catalysts measured using ICP-MS and ICP-OES. The solid line denotes perfect equality between the two measurement techniques.



**Figure 8.** Scatter plots of La, Ce, Nd, Sm, Eu and Co concentrations in seven FCC catalysts measured using ICP-MS and INAA. The solid line denotes perfect equality between the two measurement techniques. Symbols of different colors depict various catalysts employed.



**Figure 9.** REE concentrations in 25 PM<sub>2.5</sub> samples collected in Houston's Ship Channel area.



**Figure 10.** Comparison of REE concentrations in ambient PM<sub>2.5</sub> and a spent FCC catalyst

**Potential reviewers.** The following academicians can potentially review this manuscript. Please note that I do not have personal or professional relationships with them.

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